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(54) Title: LOW TEMPERATURE FLUOROCARBON ELASTOMERS				
(57) Abstract				
A fluorocarbon polymer which includes: repeating units derived from one or more perfluorinated ethers of the formula $\text{CF}_2=\text{CFO}-(\text{CF}_2)_m-(\text{O}(\text{CF}_2)_p)_n-\text{OR}_f^1$ wherein R_f^1 is a perfluorinated (C_1 - C_4) alkyl group, $m=1-4$, $n=0-6$, and $p=1-2$; and repeating units derived from vinylidene fluoride; wherein the polymer has a glass transition temperature of -50°C or lower and an oxygen to carbon ratio of at least about 0.2.				

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LOW TEMPERATURE FLUOROCARBON ELASTOMERS

Field of the Invention

This invention relates to the preparation of fluorocarbon polymeric and
10 cured elastomeric materials containing perfluoroether units, particularly repeating units
derived from perfluoroalkylvinyl ether compounds.

Background of the Invention

Fluorocarbon elastomers are synthetic elastomeric polymers with a high
15 fluorine content. See, for example, W.M. Grootaert et al., "Fluorocarbon Elastomers",
Kirk-Othmer, Encyclopedia of Chemical Technology, Vol 8, pp. 900-1005 (4th ed., John
Wiley & Sons, 1993). Fluorocarbon elastomers, particularly the copolymers of vinylidene
fluoride (VF2) with other ethylenically unsaturated halogenated monomers, such as C₃F₆
(hexafluoropropylene or HFP), have become the polymers of choice for high temperature
20 applications, such as seals, gaskets, and linings, especially when shaped articles thereof are
subject to exposure to aggressive or harsh environments, such as solvents, lubricants, and
oxidizing or reducing conditions. See, for example, U.S. Patent No. 4,912,171 (Grootaert
et al.), which discloses a fluoroelastomeric polymer prepared from VF2, tetrafluoroethylene
(TFE), and a copolymerizable hydrocarbon olefin.

25 A major drawback to many applications of shaped articles made of such
fluorocarbon elastomers has been their inability to satisfactorily function at low
temperatures. Typically, at temperatures only slightly below 0°C, shaped articles made
from copolymers of VF2 and HFP become stiff and fail to perform satisfactorily.

Low temperature flexibility of VF2 elastomers may be improved by
30 substituting perfluoro(alkyl vinyl ethers) for the HFP in VF2/HFP/TFE copolymers as
discussed in U.S. Patent No. 5,214,106 (Carlson et al.). Polymers of perfluorovinyl ethers
or copolymers with TFE are also discussed in U.S. Patent No. 3,817,960 (Resnick).

Cured perfluoroelastomers may be provided that exhibit enhanced low temperature properties through the incorporation by conventional compounding techniques of a selected perfluoropolyether into the perfluoroelastomer compound as discussed in U.S. Patent No. 5,268,405 (Ojakaar et al.). A higher than normal loading of such additives may be accomplished by using a compatibility extender such as discussed in U. S. Patent No. 3,632,788 (Stivers et al.). These additives are not permanently incorporated into the polymers and can be lost during post treatment and use of the shaped articles.

Many other fluorinated ethers have been described in the literature. One type is characterized by one of several homopolymeric segments or blocks of repeating units of the formula -CF(CF₃)CF₂-O- made from hexafluoropropylene oxide. Another type is that characterized by blocks of repeating units of the formula -CF₂CF₂-O- made from tetrafluoroethylene oxide. Others, made by reacting oxygen with tetrafluoroethylene or hexafluoropropylene, are characterized by a backbone of repeating -CF₂O-, -CF(CF₃)CF₂O-, or -CF(CF₃)O- units, a backbone of randomly distributed -CF₂O- and -CF₂CF₂O- units, a backbone of -CF(CF₃)CF₂O- and -CF₂CF₂O- units and optionally -CF₂O- and -CF(CF₃)O- units. Another type of fluorinated ether is that characterized by backbone units of the formula -(CF₂)_aO(CF₂)_b- made by photopolymerization.

A peroxide-vulcanizable, fluorine-containing elastomer can be attained by copolymerizing a perfluoro(vinylether) compound represented by the general formula: CF₂=CFO(CF₂CF(CF₃)O)_m(CF₂)_nX, wherein X is a bromine atom or an iodine atom and m and n each are 1, 2 or 3; and a fluorine-containing olefin having 2 to 8 carbon atoms in the presence of an iodine and bromine-containing compound represented by the general formula: RBr_nI_m, wherein R is a fluorohydrocarbon group, a chlorofluorohydrocarbon group, a chlorohydrocarbon group or a hydrocarbon group, and n and m each are 1 or 2 as disclosed in U.S. Patent No. 5,225,504 (Tatsu et al.).

None of these materials, however, have sufficient low temperature flexibility, particularly flexibility at temperatures as low as -50°C or lower.

Summary of the Invention

The present invention provides a fluorocarbon polymer which includes: repeating units derived from one or more perfluorinated ethers of the formula

$\text{CF}_2=\text{CFO}-(\text{CF}_2)_m-(\text{O}(\text{CF}_2)_p)_n-\text{OR}_f^1$ wherein R_f^1 is a perfluorinated ($\text{C}_1\text{-}\text{C}_4$)alkyl group, $m = 1\text{-}4$, $n = 0\text{-}6$, and $p = 1\text{-}2$; and repeating units derived from vinylidene fluoride; wherein the polymer has a glass transition temperature of -50°C or lower and an oxygen to carbon ratio of at least about 0.2. Preferably, when m is 2 or 3 in the above formula, n is not 0.

5 The fluorocarbon polymer preferably further includes an effective amount (preferably, 0.2-5 mole-%) of cure site moieties derived from one or more compounds of the formulae: a) $\text{CX}_2=\text{CX}(\text{Z})$, wherein: (i) X is H or F; and (ii) Z is Br, I, or R_f^2U wherein $\text{U} = \text{Br}, \text{I}, \text{or CN}$ and $\text{R}_f^2 =$ a perfluorinated divalent linking group optionally containing O atoms; and (b) $\text{Y}(\text{CF}_2)_q\text{Y}$, wherein: (i) Y is Br or I; and (ii) $q = 1\text{-}6$.

10 The present invention also provides an elastomeric polymer prepared from a crosslinkable composition comprising a fluorocarbon polymer as described above. The crosslinkable composition can further include a free radical initiator, such as a peroxide initiator, a co-curing agent, such as a triallyl isocyanurate, and/or one or more fillers. The elastomeric polymer can be used to make seals, hoses, diaphragms, coatings, etc.

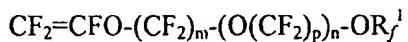
15 The present invention further provides methods of preparing an elastomeric polymer as described above. A preferred method includes: (a) providing a crosslinkable composition comprising a fluorocarbon polymer, the polymer comprising: i) repeating units derived from one or more perfluorinated ethers of the formula (Formula I):
 $\text{CF}_2=\text{CFO}-(\text{CF}_2)_m-(\text{O}(\text{CF}_2)_p)_n-\text{OR}_f^1$ wherein R_f^1 is a perfluorinated ($\text{C}_1\text{-}\text{C}_4$)alkyl group, $m = 1\text{-}4$, $n = 0\text{-}6$, and $p = 1\text{-}2$; ii) repeating units derived from vinylidene fluoride; and iii) 0.2-5 mole-% of cure site moieties derived from one or more compounds of the formulae: $\text{CX}_2=\text{CX}(\text{Z})$, wherein: X is H or F; and Z is Br, I, or R_f^2U wherein $\text{U} = \text{Br}, \text{I}, \text{or CN}$ and $\text{R}_f^2 =$ a perfluorinated divalent linking group optionally containing O atoms; and $\text{Y}(\text{CF}_2)_q\text{Y}$, wherein: Y is Br or I; and $q = 1\text{-}6$; wherein the polymer has a glass transition temperature of -50°C or lower and an oxygen to carbon ratio of at least about 0.2; and (b) subjecting the crosslinkable composition to conditions effective to at least partially cure it. Preferably, the step of subjecting the crosslinkable composition to conditions effective to at least partially cure it includes applying heat and pressure and/or subjecting the composition to radiation.

Detailed Description of the Invention

The present invention relates to the preparation of fluorocarbon polymers, particularly curable fluorocarbon polymers having cure site, cured elastomers, and the processes for their curing. These materials have a variety of uses. The fluorocarbon polymers can be cured to provide fluorocarbon elastomers for use in seals, gaskets, hoses, diaphragms, linings, and other shaped articles, that have improved performance characteristics, particularly flexibility, at low temperatures. They can also be used as coatings. Even if not cured, these materials can be used in caulk or as diluents in thermoplastics, for example, to provide enhanced low temperature properties.

10 Preferably, the fluorocarbon polymers are prepared from perfluoroalkylvinyl ether and vinylidene fluoride, and have a Tg of less than about -50°C, and more preferably, less than about -60°C. Herein, particularly in the claims, Tg is defined as the midpoint on the curve obtained from a differential scanning calorimeter (DSC) analysis of the polymer using ASTM E1356-91 (Reapproved 1995). For certain of
15 the examples in the Examples Section, the Tg values are slightly lower than would be obtained if this method were used. These values were obtained using Russian Standard Method 12254-66, which defines Tg as the start of deformation on defrosting a sample under a 5 kg load. Such values are typically 5-10°C lower than if the ASTM method were used.

20 The present invention provides a fluorocarbon polymer (preferably, a curable fluorocarbon elastomer) that includes repeating units (i.e., interpolymerized units) derived from vinylidene fluoride and a perfluorinated ether of the formula (Formula I):



25 wherein R_f¹ is a perfluorinated (C₁-C₄)alkyl group, m = 1-4 (preferably m=2-4, and more preferably 2 for certain embodiments, and 1-2 for other embodiments) and n = 0-6 (preferably 1-5, and more preferably 2-4), and p = 1-2 (preferably, 1). For certain aspects of the invention, if m>2, then n is preferably at least 1. These perfluorinated ethers are also referred to herein as perfluoroalkoxyalkylvinylethers ("PAAVE"). Reference is made to
30 *The Role of the Reactor Surface in the Liquid-Phase Oxidation of Hexafluoropropylene,*

S. V. Kartsov, P. I. Valov, L. F. Sokolov, and S. V. Sokolov, Institute of Chemical Physics, Academy of Sciences of the USSR, Moscow, translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 10, pp. 2268-2272, October, 1978, as well as U.S. Pat. Nos. 3,817,960 (Resnick) and 5,696,216 (Kruger et al.) in relation to the production 5 of the compounds of Formula I.

The perfluorinated ether of Formula I has no pendant alkyl groups (e.g., -CF(CF₃)-CF₂-O-) which can reduce the low temperature flexibility of the cured material. The fluorocarbon polymer also has an oxygen to carbon ratio of at least about 0.2, which has been discovered to play a significant role in the low temperature properties of the final 10 cured elastomeric material.

The oxygen to carbon ratio (O/C) is determined by dividing the total moles of oxygen in the polymer by the total moles of carbon atoms in the polymer. The higher the oxygen to carbon ratio, the more desirable the low temperature characteristics of the cured elastomer. Specifically, the higher the O/C ratio, the lower the glass transition temperature 15 (T_g), which results in a lower temperature at which the polymer is still elastic, and a lower temperature at which the cured elastomer is still flexible. However, the effect of varying the O/C ratio is qualitative and not quantitative because the T_g may be affected by a number of other factors. Such factors include overall molecular weight, and the presence of optional comonomers, such as TFE, and the length of the unit blocks of the comonomers.

There are at least two ways to alter the O/C ratio, which can be used in combination. One way in which the O/C ratio can be increased is to increase the length of any pendant groups, which are typically oxygen-containing alkyl groups, of the polymer by adding perfluoroalkoxy fragments high in oxygen atoms. Another way is to increase the mole percent of the perfluoroalkoxyallylvinylethers that are high in oxygen atoms in the 20 total composition. The most effective way of increasing the O/C ratio, however, is to increase the quantity of perfluoromethylvinyl ether (-CF₂O-) or perfluoroethylvinyl ether (-CF₂CF₂O-) segments in the vinyl ether. The use of perfluoropropylvinyl ethers are less effective in increasing the O/C ratio.

Examples of suitable fluorocarbon polymers of Formula I are listed in the 30 following Table 1 along with the T_g and O/C ratio ($m + n = 1$).

Table 1



Example	R	m	Tg ¹ degrees C	O/C Ratio ²
#	Group			
1	-OCF ₂ CF ₂ OCF ₂ OCF ₃	0.3	-70	0.25
2	-OCF ₂ CF ₂ -(OCF ₂) ₄ -OCF ₃	0.3	-95	0.40
3	-OCF ₂ CF ₂ (OCF ₂ CF ₂) ₄ OCF ₃	0.2	-70	0.29
4	-OCF ₂ CF ₂ (OCF ₂ CF ₂) ₄ OCF ₃	0.3	-75	0.34
5	-OCF ₂ CF ₂ (OCF ₂ CF ₂) ₄ OCF ₃	0.4	-80	0.37
6	-OCF ₂ CF ₂ -(OCF ₂) ₂ -OCF ₃	0.2	-75	0.27
7	-OCF ₂ CF ₂ -(OCF ₂) ₂ -OCF ₃	0.3	-79	0.34
8	-OCF ₂ CF ₂ -(OCF ₂) ₂ -OCF ₃	0.4	-86	0.40
9	-OCF ₂ CF ₂ -(OCF ₂) ₄ -OCF ₃	0.2	-91	0.35
10	-OCF ₂ CF ₂ -(OCF ₂) ₄ -OCF ₃	0.3	-100	0.44
11	-OCF ₂ CF ₂ -(OCF ₂) ₄ -OCF ₃	0.4	-109	0.50
12	-OCF ₂ CF ₂ -(OCF ₂) ₆ -OCF ₃	0.2	-90	0.42
13	-OCF ₂ CF ₂ -(OCF ₂) ₆ -OCF ₃	0.3	-107	0.51
14	-OCF ₂ CF ₂ -(OCF ₂) ₆ -OCF ₃	0.4	-119	0.66

¹Determined using Russian Standard Method 12254-66 (accuracy 3°C)

5 ²O/C ratio = [Number of O atoms x fraction of CF₂=CF-R] / [(Number of C atoms in VF2
x fraction of VF2) + (Number of C atoms in CF₂=CF-R x fraction of CF₂=CF-R)]

The fluorocarbon polymers of the present invention without curing are
useful in a variety of applications. However, they are particularly advantageous because
10 they can be cured to form elastomers having significant low temperature properties (e.g.,
flexibility). They can be cured by a variety of techniques. Preferably, however, the
polymers include a halogen (typically, bromine and iodine) cure site or a nitrile cure site
within the molecule.

Thus, preferably, and advantageously, the fluorocarbon polymer includes
15 repeating units derived from a perfluorinated ether of the formula

$\text{CF}_2=\text{CFO}-(\text{CF}_2)_m-(\text{O}(\text{CF}_2)_p)_n-\text{OR}_f^1$ wherein R_f^1 is a perfluorinated ($\text{C}_1\text{-}\text{C}_4$)alkyl group, $m = 1\text{-}4$, $n = 0\text{-}6$, and $p = 1\text{-}2$, repeating units derived from vinylidene fluoride, and an effective amount (i.e., an amount effective to provide a cured elastomer) of cure site moieties

derived from one or more compounds containing a halogen or a nitrile moiety. Cure site
5 moieties used in the invention may have pendant groups, such as alkyl moieties, if desired.

Examples of such compounds useful in providing the cure site moiety are described in U.S. Pat. Nos. 5,696,216 (Kruger et al.) and 5,679,851 (Saito et al.). Preferably, the cure site moieties are derived from one or more compounds of the formulae: $\text{CX}_2=\text{CX}(\text{Z})$, wherein X is H or F (preferably, F), Z is Br, I, or R_f^2U wherein U = Br, I, or CN, and R_f^2 is a

10 perfluorinated divalent linking group optionally containing O atoms; and $\text{Y}(\text{CF}_2)_q\text{Y}$,

wherein Y is Br or I and q = 1-6. Preferably, there are about 0.2-5 mole-% of these cure site moieties present. A preferred group of cure site moieties include those derived from compounds such as $\text{CF}_2=\text{CFBr}$, $\text{CF}_2=\text{CHBr}$, $\text{CF}_2=\text{CHCF}_2\text{CF}_2\text{Br}$, $\text{ICF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{I}$,

$\text{BrCF}_2\text{CF}_2\text{Br}$, $-\text{CF}_2=\text{CFO}(\text{CF}_2)_3-\text{OCF}_2\text{CF}_2\text{Br}$, and mixtures thereof. Such compounds may

15 be produced as described in U.S. Pat. Nos. 4,418,186 (Yamabe et al.), 5,225,504 (Tatsu et al.), and 5,214,106 (Carlson et al.). Another preferred group of cure site moities include those derived from compounds such as $\text{CF}_2=\text{CFO}(\text{CF}_2)_r\text{OCF}(\text{CF}_3)_s\text{CN}$ wherein r = 2-5.

Such compounds may be produced as described in U.S. Pat. Nos. 5,679,851 (Saito et al.), 5,717,037 (Saito et al.), and 5,736,614 (Saito et al.), and Synthesis of Fluoroorganic

20 Compounds Monomers and Intermediate Products, Academician I.L. Knunyanc and Prof. G.G. Yakobson, Moscow, Izdatelstvo, "Chimia" 1997.

Preferably, the fluorocarbon polymers of the present invention include about 50-80 mole-% of the repeating units derived from vinylidene fluoride, and about 10-50 mole-% of the repeating units derived from the perfluorinated ether, with or without a

25 halogen cure site. They can optionally include up to about 30 mole-% of repeating units derived from a fluoromonoolefin other than the perfluorinated ether and vinylidene fluoride. Such other fluoromonoolefins include, for example, hexafluoropropene, chlorotrifluoroethylene, tetrafluoroethylene, 1-hydropentafluoropropene, perfluoro(methylvinylether) perfluoro(propylvinylether), perflourocyclobutene, and
30 perfluoro(methylcyclopropene). Optionally, the aforementioned one or more

fluoromonoolefins may be copolymerized with fluorine-free olefinic monomers such as ethylene and propylene.

The preferred elastomers are copolymers of vinylidene fluoride, a compound of Formula I, and at least one terminally unsaturated fluoromonoolefin containing at least one fluorine atom substituent on each double-bonded carbon atom, each carbon atom of said fluoromonoolefin being substituted only with fluorine, chlorine, hydrogen, lower fluoroalkyl radical, or lower fluoroalkoxy radical, particularly hexafluoropropene, tetrafluoroethylene, chlorotrifluoroethylene, and 1-hydropentafluoropropene. When including other copolymerizable monomers, such as tetrafluoroethylene (TFE), and retention of the superior low temperature properties is desired, the monomers should be included in quantities and unit blocks which do not substantially alter the low temperature properties.

The present invention also provides an elastomeric polymer prepared from a crosslinkable composition comprising the curable fluorocarbon polymer described above.

For compounds containing halide cure site moieties, the crosslinkable composition can further include an optional free radical initiator, and an optional co-curing agent. Although such additives are preferred, they are not necessarily required, as crosslinking can also occur through the use of e-beam radiation, for example.

Preferably, the free radical initiator is a peroxide. Such peroxide curatives include organic or inorganic peroxides. Organic peroxides are preferred, particularly those that do not decompose during dynamic mixing temperatures. Suitable peroxides include dicumyl peroxide, 2,5-dimethyl-2,5-di(t-butylperoxy)hexane, di-t-butyl peroxide, t-butylperoxy benzoate, 2,5-dimethyl-2,5-di(t-butylperoxy)hexane-3 and laurel peroxide. Other suitable peroxide curatives are listed in U.S. Patent No. 5,225,504 (Tatsu et al.).

The amount of peroxide curing agent used generally will be 0.1 to 5, preferably 1 to 3 parts per 100 parts of fluoropolymer gum (i.e., fluorocarbon polymer).

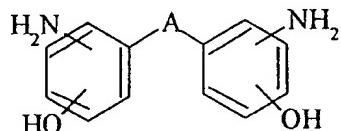
In peroxide vulcanization of the fluorocarbon polymer using an organic peroxide, it is often desirable to include a co-curing agent (e.g., a co-agent or co-crosslinking agent). The use of such a co-curing agent is well known to one skilled in the art. Examples of such agents include tri(methyl)allyl isocyanurate, triallyl isocyanurate, tri(methyl)allyl cyanurate, N,N'-m-phenylene bismaleimide, diallyl phthalate,

tris(diallylamine)-s-triazine, triallyl phosphite, 1,2-polybutadiene, ethyleneglycol diacrylate, diethyleneglycol diacrylate, etc. Another useful co-curing agent may be represented by the formula $\text{CH}_2=\text{CH}-\text{R}_Y^1-\text{CH}=\text{CH}_2$ wherein R_Y^1 is as described above. Such co-curing agents provide enhanced mechanical strength to the final cured elastomer. They generally are used in amount of 1 to 10, preferably 1 to 5 parts, per 100 parts of the fluorocarbon polymer.

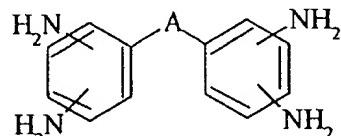
For nitrile cure site moieties, the crosslinkable composition can further include one or more substances known to promote the formation of triazine rings by trimerization of nitriles under the influence of heat. These include organometallic compounds of arsenic, antimony, and tin described in U.S. Patent Nos. 3,470,176 (Zollinger et al.) and 3,546,186 (Gladding et al.), and the metal oxides described in U.S. Patent No. 3,523,118 (Emerson et al.).

Other compounds that can be used to vulcanize fluorocarbon polymers containing nitrile cure site moieties include bis(aminophenols) of the formula

15



and tetraamines of the formula



20 where A is SO_2 , O, CO, ($\text{C}_1\text{-R}_6$) alkyl groups, perfluoro ($\text{C}_1\text{-C}_{10}$) alkyl groups, or a carbon-carbon bond linking the two aromatic rings. Such compounds are disclosed in U.S. Patent No. 4,525,539 (Feiring). Other vulcanizers or promoters that can be used in compositions containing fluorocarbons polymers having nitrile cure sites are disclosed in U.S. Patent Nos. 4,005,142 (Evers) and 4,434,106 (Rosser et al.).

25 A further optional component (a preferred component for compounds containing halide cure site moieties) in the crosslinkable composition is an acid acceptor.

Acid acceptors can be inorganic or organic compounds. Organic acid acceptors include sodium stearate and magnesium oxalate. However, acid acceptors are generally inorganic bases and include magnesium oxide, lead oxide, calcium oxide, calcium hydroxide, dibasic lead phosphite, zinc oxide, barium carbonate, strontium hydroxide, calcium carbonate, etc.

- 5 The preferred acid acceptors are zinc oxide and calcium hydroxide. The acid acceptors can be used singly or in combination, and are used in amounts ranging from about 1 to about 25 parts per 100 parts by weight of the polymer.

The crosslinkable composition can also include fillers and colorants. Fillers can be mixed with the fluorocarbon polymer to improve molding characteristics and other 10 properties. When a filler is employed, it can be added to the vulcanization recipe in amounts of up to about 100 parts per hundred parts by weight of fluorocarbon polymer, preferably between about 15 to 50 parts per hundred parts by weight of the fluorocarbon polymer. Examples of fillers which may be used include, but are not limited to, reinforcing thermal grade carbon blacks or non-black pigments of relatively low reinforcement 15 characteristics such as clays and barytes.

The crosslinkable fluorocarbon polymer composition can be compounded or mixed in one or several steps, using any of the usual rubber mixing devices such as internal mixers (e.g., Banbury mixers), roll mills, etc. For best results, the temperature of the mixture should not rise above about 120°C. During mixing it is necessary to distribute the 20 components and additives uniformly throughout for effective cure.

The mixture is then processed and shaped, for example, by extrusion (for example in the shape of a hose or hose lining) or molding (for example, in the form of an O-ring seal). The shaped article can then be heated to cure the gum composition and form a cured elastomer article.

25 Pressing of the compounded mixture (i.e., press cure) is typically conducted at a temperature of about 95-230°C, preferably about 150-205°C, for a period of about 1 minute to about 15 hours, usually for about 1-10 minutes. A pressure of about 700-20,000 kPa, preferably about 3400-6800 kPa, is typically used in molding the composition. The molds first may be coated with a release agent and prebaked.

30 The molded vulcanizate is then usually post cured in an oven at a temperature of about 150-315°C, preferably at a temperature of about 200-260°C, for a

period of about 2-50 hours or more, depending on the cross-sectional thickness of the sample. For thick sections, the temperature during the post cure is usually raised gradually from the lower limit of the range to the desired maximum temperature. The maximum temperature used is preferably about 260°C, and is held at this value for about 4 hours or
5 more.

The invention will be further described by reference to the following detailed examples. These examples are offered to further illustrate the various specific and illustrative embodiments and techniques. It should be understood, however, that many variations and modifications may be made while remaining within the scope of the present
10 invention.

Examples

The following examples describe the preparation and evaluation of elastomeric copolymer materials containing perfluoroether units and cured compositions of
15 the invention. The indicated results were obtained using the following test methods:

Test Methods

Mooney viscosity was determined by ASTM 1646-94 (ML 1+ 10 @ 121°C). Results are reported in Mooney units.

Cure Rheology Tests were run on uncured, compounded admixtures using a Monsanto Moving Die Rheometer (MDR) Model 2000 in accordance with ASTM D 5289-95 at 177°C, no preheat, 12 minute elapsed time (unless otherwise specified) and a 0.5° arc. Minimum torque (M_L), Maximum torque (M_H), i.e., highest torque attained during specified period of time when no plateau or maximum was obtained and Difference in
20 Torque, ΔT , i.e., ($M_H - M_L$), were reported. Also reported were: $t_{\Delta 2}$ (time for torque to increase 2 units above M_L), $t'50$ (time for torque to reach $M_L + 0.5[M_H - M_L]$), and $t'90$ (time for torque to reach $M_L + 0.9[M_H - M_L]$).
25

Press-cured samples (150 x 75 x 2.0 mm sheets, unless otherwise noted) were prepared for physical property determination by pressing at about 6.9×10^3 kPa for
30 the indicated amount of time and temperature.

Post cure samples were prepared by placing a press-cured sample in a circulating air oven. The oven was maintained at 232°C and the samples treated for 16 hours.

- Tensile Strength at Break, Elongation at Break, and Modulus at 100%
5 Elongation were determined using ASTM D 412-75 on samples cut from 2.0 mm sheet with ASTM Die D. Units are reported in Mega Pascals (MPa).

Hardness was determined using ASTM D 2240-85 Method A with a Type A-2 Shore Durometer. Units are reported in points.

- Retraction at Lower Temperatures (TR-10) was determined using ASTM
10 D1329-88 (reapproved 1993) with ethanol as the cooling media. Units are reported in °C.

Compression set determined by ASTM D 395-89 Method B with 0.139 inch (3.5 mm) O-rings compressed for 70 hours at 200°C. Results are reported as %.

Glass Transition Temperature

- 15 Glass Transition Temperature was determined by ASTM E1356-91 (Reapproved 1995), or by Russian Standard Method 12254-66, which is briefly described below. This was measured using a static load. A rubber cylinder was cooled at a rate of 1-5 degrees/minute to the temperature 10-20 degrees below the expected glass transition temperature. The temperature was maintained until the sample froze which typically took
20 about 10 minutes. A load of 5 kg was then applied and the samples were heated at a rate of 1 degree/minute. The temperature and strain was registered every minute. The temperature where a regular increase in deformation started was taken as the glass transition temperature. An average of 5-10 measurements were taken.

Copolymer 1

- Copolymer 1 was made in a 1 liter stainless steel reactor equipped with magnetic-driven stirrer (3000 rpm), two precision valves for feeding in the reaction components, siphon for sampling, thermocouple, vacuum gage and a thermostatically controlled jacket. The reactor was evacuated and charged with 225 grams of deionized
30 water. The following ingredients were then added from a glass ampule: 92 grams of CF₂=CFOCF₂CF₂(OCF₂)₄OCF₃ (ether); 2.0 grams of CF₂=CFOCF₂CF₂CF₂OCF₂CF₂Br

(halogen cure site); and 0.45 gram of initiator $[CF_3CF_2CF_2OCF(CF_3)COO]_2$ in 6.9 grams of Freon 113 solution were charged into the reactor. Then, while stirring, 23.8 grams of TFE monomer and 30.1 grams of VF2 monomer were fed from a metallic cylinder. A molar ratio of the charged monomers was 53.6 / 26.7 / 19.2 / 0.5, respectively, of VF2 / TFE / ether / halogen cure site.

The reactor was heated to 24°C and the pressure in the reactor rose to 16 atm. The polymerization was carried out at 21-22°C. The pressure decreased as polymerization proceeded, and the process was stopped when the pressure reached a constant 1.3 atm. The reactor was cooled to room temperature, the stirring was stopped, and the gaseous substances were purged. The reactor was opened and the copolymer which had all coagulated in the course of polymerization was separated. The copolymer was washed thoroughly with hot water, then washed once with ethanol and dried at 60°C. A yield of 130 grams of copolymer was obtained. The properties of Copolymer 1 are given in Table 2.

15

Copolymer 2

Copolymer 2 was made in a 1 liter stainless steel reactor equipped with magnetic-driven stirrer (3000 rpm), two precision valves for feeding in the reaction components, siphon for sampling, thermocouple, vacuum gage, and a jacket connected to a thermostat. The reactor was evacuated and charged with 230 grams of deionized water. The following ingredients were then charged into the reactor from a glass ampule: 93.6 grams of $CF_2=CFOCF_2CF_2(OCF_2)_4OCF_3$ (ether), 1.98 grams of $CF_2=CFOCF_2CF_2OCF_2CF_2Br$ (halogen cure site), and 0.45 gram of initiator $[CF_3CF_2CF_2OCF(CF_3)COO]_2$ in 6.9 grams of Freon 113 solution were. Then, while stirring, 24.0 grams of TFE monomer and 30.7 grams of VF2 monomer were fed from a metallic cylinder. A molar ratio of the charged monomers was 53.6 / 26.7 / 19.2 / 0.5 respectively of VF2 / TFE / ether / halogen cure site.

The reactor was heated to 24°C and the pressure in the reactor rose to 17 atm. The polymerization was carried out at 21-24°C. The pressure decreased as polymerization proceeded, and the process was stopped when the pressure reached a constant 2.6 atm. The reactor was cooled to room temperature, the stirring was stopped,

and the gaseous substances were purged. The reactor was opened and the copolymer which had all coagulated in the course of polymerization was separated. The copolymer was washed thoroughly with hot water, then washed once with ethanol and dried at 60°C under vacuum. A yield of 110 grams of copolymer was obtained. The properties of 5 Copolymer 2 are in Table 2.

Copolymer 3

Copolymer 3 was made in a 40 liter stainless steel reactor equipped with a safety valve for 40 kg/cm² pressure, jacket for temperature control, stirrer rotating at 180 10 to 220 rpm, a siphon for charging monomers, thermocouple, vacuum gage and a bottom discharge valve. The reactor was evacuated and charged with 22.1 kg of deionized water, 1.4 kg of Freon 113, and 8.0 grams of [CF₃CF₂CF₂OCF(CF₃)COO]₂ in 39 grams of Freon 113. Then, while stirring, a mixture of 3.25 kg of VF₂, 1.55 kg of TFE, 7.27 kg of CF₂=CFOCF₂CF₂(OCF₂)₃OCF₃, and 0.065 kg of CF₂=CFBr was added from a stainless 15 steel cylinder over one hour while maintaining the temperature at 30°C and the pressure at 17.5 atm. The molar ratio of charged monomer was 61.7/19.1/18.7/0.5, respectively, of VF₂/TFE/ether/halogen cure site. The reaction was allowed to proceed at temperature until the pressure dropped to 1 atm. Total reaction time was 19 hours.

The reactor was cooled to room temperature and the gaseous substances 20 were purged. The reactor was opened and the copolymer, which had all coagulated in the course of the polymerization was separated. The copolymer was washed thoroughly with hot water (70°C) and then dried under vacuum at 60°C. A yield of 7.7 kg of copolymer was obtained. The properties of Copolymer 3 are given in Table 2.

25 Copolymer 4

Copolymer 4 was made in a 40 liter stainless steel reactor equipped with a safety valve for 40 kg/cm² pressure, jacket for temperature control, stirrer rotating at 180 to 220 rpm, a siphon for charging monomers, thermocouple, vacuum gage and a bottom discharge valve. The reactor was evacuated and charged with 22.1 kg of deionized water, 30 1.4 kg of Freon 113, and 8.0 grams of [CF₃CF₂CF₂OCF(CF₃)COO]₂ in 39 grams of

Freon 113. Then, while stirring, a mixture of 3.25 kg of VF₂, 1.55 kg of TFE, 7.27 kg of CF₂=CFOCF₂CF₂(OCF₂)₃OCF₃, and 0.065 kg of CF₂=CFBr was added from a stainless steel cylinder over one hour while maintaining the temperature at 35°C and the pressure at 17.5 atm. The molar ratio of charged monomer was 61.7/19.1/18.7/0.5, respectively, of 5 VF₂/TFE/ether/halogen cure site. The reaction was allowed to proceed at temperature until the pressure dropped to 1 atm. Total reaction time was 16 hours.

The reactor was cooled to room temperature and the gaseous substances were purged. The reactor was opened and the copolymer, which had all coagulated in the course of the polymerization was separated. The copolymer was washed thoroughly with 10 hot water (70°C) and then dried under vacuum at 60°C. A yield of 9.7 kg of copolymer was obtained. The properties of Copolymer 4 are given in Table 2.

Table 2

<u>Polymer</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
Tg(a), °C	-92	-90	-83	-81
Tg(b), °C	-80	-80	-78	-72
O/C Ratio	0.33	0.31	0.28	0.28
Mooney Viscosity	35	29	37	48
<u>Composition, Mole %</u>				
VF ₂	53.6	55.5	58.8	61.8
TFE	28.0	28.0	23.7	20.9
Ether	18.0	16.0	17.0	16.7
CSM	0.4	0.5	0.5	0.6

- a) By Russian Standard Method 12254-66
 b) By ASTM E1356-91 at a Scan Rate of 20°C/min

Examples 1-4

In the following examples, the compositions are based on 100 parts of copolymer. The curatives and other additives are listed as parts per hundred parts of the rubber or copolymer (phr). The formulations and test results are summarized in Table 3.

Table 3
Compound Evaluation

Polymer				
#1	100			
#2		100		
#3			100	
#4				100
ARO-60 ¹	30	30		
N-990 ²			30	30
Ca(OH) ₂ ³	3	3	3	3
TAIC ⁴	3	2	1.5	1.5
Luperco 101XL ⁵	3	2	1.5	1.5

10 **Monsanto MDR at 177°C, 0.5° Arc, 100 cpm, 12 Minutes**

ML, dNm	2.1	2.3	2.0	1.7
MH, dNm	10.9	9.6	9.9	9.0
ΔT, dNm	8.8	7.3	7.9	7.3
T _{S2} , min	0.8	1.1	0.6	0.7
t'50, min	1.1	1.4	0.8	0.9
t'90, min	3.6	4.4	2.0	2.5

Properties, 2mm Thick Sheet, Die D Dumbbells

Press Cure Time, min @ 177°C	10 min	10 min	10 min	10 min
Post Cured 16 hrs @ Temp.	230°C	200°C	230°C	230°C
Tensile, Mpa	6.3	6.7	5.5	6.7
100% Mod, Mpa	2.4	1.2	3.4	4.0
Elongation, %	205	475	135	130
Hardness, Shore A2	58	61	60	57

Compression Set, Method B, O-Rings

70 hr @ 200°C	38	50	20.5	16.7
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MEOH Volume Swell, One (1) Week at Room Temp

%	4.6	4.6	8	7
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Temperature of Retraction, ASTM D-1329 (50% of Break Elongation)

(In ETOH)

TR-2, °C	-75.5	-75.6	-71	-69
TR-10, °C	-69.9	-68.6	-57	-61
TR-30, °C	-43.8	-41.7	-39	-43
TR-50, °C	-22.9	-21.0	-22	-24
TR-50, °C	-4.8	-9.0	-3	-6
Tensile Set, %	4	--	2.0	1.0

¹ Carbon black obtained from J.M. Huber Corp., Borger, TX

10 ² Carbon black obtained from J.M. Huber Corp., Borger, TX

³ Obtained from C.P. Hally Bedford Park, IL

⁴ Trialkyisocyanurate obtained from Mitsubishi Industry, Tokyo, JP

⁵ Peroxide obtained from Lucidol Division of Pennwalt Corp., Buffalo, NY

15 Copolymer 5

Copolymer 5 was made in a 40 liter stainless steel reactor equipped with a safety valve for 40 kg/cm² pressure, jacket for temperature control, stirrer rotating at 180 to 220 rpm, a siphon for charging monomers, thermocouple, vacuum gage and a bottom discharge valve. The reactor was evacuated and charged with 13 kg of deionized water and an aqueous solution of 60/40 weight ratio of ammonium perfluoroheptanoate and ammonium perfluorooctanoate containing 190 grams of total surfactants. An aqueous solution of 13 grams of ammonium persulfate was then added. Then, while stirring, a mixture of 2.1 kg of VF₂, 4.27 kg of CF₂=CFOCF₂CF₂(OCF₂)₂OCF₃ and 0.17 kg of CF₂=CFO(CF₂)₃OCF(CF₃)CN was added from a stainless steel cylinder. The molar ratio

of the charged monomers was 75.3/23.7/1.0, respectively, of VF₂/ether/nitrile cure site.

The temperature was then increased to 60°C resulting in a pressure of 28.7 atm. The reaction proceeded until the pressure dropped to 1 atm. Total reaction time was 12 hours.

The reactor was cooled to room temperature and the gaseous substances were purged. The latex was removed through the bottom discharge valve, coagulated with MgCl₂ solution; washed with hot water (70°C) and dried under vacuum at 60°C. A yield of 4.0 kg of polymer was obtained. The properties of Copolymer 5 are given in Table 4.

Copolymer 6

Copolymer 6 was made in a 40 liter stainless steel reactor equipped with a safety valve for 40 kg/cm² pressure, jacket for temperature control, stirrer rotating at 180 to 220 rpm, a siphon for charging monomers, thermocouple, vacuum gage and a bottom discharge valve. The reactor was evacuated and charged with 13 kg of deionized water and an aqueous solution of 60/40 weight ratio of ammonium perfluoroheptanoate and ammonium perfluorooctanoate containing 190 gms of total surfactants. An aqueous solution of 13 grams of ammonium persulfate was then added. Then, while stirring, a mixture of 2.0 kg of VF₂, 4.1 kg of CF₂=CFOCF₂CF₂(OCF₂)₂OCF₃ and 0.24 kg of CF₂=CFO(CF₂)₃OCF(CF₃)CN was added from a stainless steel cylinder. The molar ratio of the charged monomers was 74.8/23.7/1.5, respectively, of VF₂/ether/nitrile cure site.

The temperature was then increased to 60°C resulting in a pressure of 23.6 atm. The reaction proceeded until the pressure dropped to 1 atm. Total reaction time was 19 hours.

The reactor was cooled to room temperature and the gaseous substances were purged. The latex was removed through the bottom discharge valve, coagulated with MgCl₂ solution; washed with hot water (70°C) and dried under vacuum at 60°C. A yield of 3.9 kg of polymer was obtained. The properties of copolymer 6 are given in Table 4.

Copolymer 7

Copolymer 7 was made in a 40 liter stainless steel reactor equipped with a safety valve for 40 kg/sq cm pressure, jacket for temperature control, stirrer rotating at 180 to 220 rpm, a siphon for charging monomers, thermocouple, vacuum gage and a bottom

discharge valve. The reactor was evacuated and charged with 21 kg of deionized water and an aqueous solution of 60/40 weight ratio of ammonium perfluoroheptanoate and ammonium perfluorooctanoate containing 315 grams of total surfactant. An aqueous solution of 21 grams of ammonium persulfate was then added. Then, while stirring and the temperature at 65°C, a mixture of 2.6 kg of VF₂, 1.1 kg of TFE, 6.5 kg of CF₂=CFOCF₂CF₂(OCF₂)₂OCF₃, and 0.39 kg of CF₂=CFO(CF₂)₃OCF(CF₃)CN was added from a stainless steel cylinder continuously. The molar ratio of the charged monomers were 59.4/16.1/23.0/1.5, respectively, VF₂/TFE/Ether/nitrile cure site. The pressure was held at 4 atms during the polymerization by controlling the rate of addition of the monomers. The reaction was stopped after all the monomer was added and the pressure had dropped to 1 atm. Total reaction time was 57 hours.

The reactor was cooled to room temperature and the gaseous substances were purged. The latex was removed through the bottom discharge valve, coagulated with MgCl₂ solution; washed with hot water (70°C) and dried under vacuum at 60°C. A yield of 6.0 kg of polymer was obtained. The properties of Copolymer 7 are given in Table 4.

Table 4

<u>Polymer</u>	<u>5</u>	<u>6</u>	<u>7</u>
Tg(a), °C	-73	-76	-79
Tg(b), °C	-66	-66	-66
O/C Ratio	0.29	0.29	0.31
Mooney Viscosity	11	4	2
<u>Composition, Mole %</u>			
VF ₂	76.2	76.2	60.0
TFE	--	--	14.2
Ether	22.7	22.5	24.0
CSM	1.1	1.3	1.8

a) By Russian Standard Method 12254-66

b) By ASTM E1356-91 at a Scan Rate of 20°C/min

Examples 5-7

In the following examples, the compositions are based on 100 parts of copolymer. The curative and other additives are listed as parts per hundred parts of the 5 rubber or copolymer (phr). The formulations and test results are summarized in Table 5.

Table 5**Compound Evaluation**

Polymer			
#5	100		
#6		100	
#7			100
N-990 ¹	40	40	40
BOAP ²	2	2	2
FC-143 ³	1		1

MDR @ X°C, 0.5°ARC, X MIN

	Minutes	30	30	30
Temperature	177	177	177	
ML, dNm	0.4	0.2	0.0	
MH, dNm	7.3	2.7	4.6	
ΔT, dNm	6.9	2.5	4.6	
t _s ² , min	6.3	28.7	9.1	
t'50, min	9.5	23.0	9.2	
t'90, min	18.3	28.7	19.0	

10

Physical Properties**Press Cure X min @ 177°C**

	Minutes	30	60	30
Tensile, Mpa	4.6	5.2	3.2	
100%, Mod, Mpa	2.0	1.3	1.2	
Elongation, %	215	390	220	
Hardness, Shore A ₂	55	--	48	

15

Post Cure 16^ohrs @ 230^oC

Tensile, Mpa	5.2	5.0	3.9
100% Mod, Mpa	4.2	4.3	3.6
Elongaton, %	110	110	105
Hardness, Shore A ₂	55	55	53

Compression Set, Method B, O-Rings

70 hr @ 200 ^o C, %	15.8	12.7	21.7
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5 Low Temperature of Retraction in Ethanol

TR-2, °C	-62	-61	-61
TR-10, °C	-58	-56	-56
TR-30, °C	-52	-50	-39
TR-50, °C	-45	-45	-42
TR-70, °C	-21	-21	-32

¹ Carbon black obtained from J.M. Huber Corp., Borger, TX.

² 2,2-Bis(3-amino-4-hydroxyphenyl)hexafluoropropane, obtained from Central Glass Co., Saitama, Japan.

10 ³ Fluorad® Surfactant, FC-143, obtained from 3M, St. Paul, MN.

The results in Tables 3 and 5 show that useful, cured samples may be made using the compositions of the invention.

15 The complete disclosure of all patents, patent documents, and publications cited herein are incorporated by reference. The foregoing detailed description and examples have been given for clarity of understanding only. No unnecessary limitations are to be understood therefrom. The invention is not limited to the exact details shown and described, for variations obvious to one skilled in the art will be included within the
20 invention defined by the claims.

WHAT IS CLAIMED IS:

1. A fluorocarbon polymer comprising:
 - a) repeating units derived from one or more perfluorinated ethers of the formula
5 (Formula I):
$$\text{CF}_2=\text{CFO}-(\text{CF}_2)_m-(\text{O}(\text{CF}_2)_p)_n-\text{OR}_f^1$$
wherein R_f^1 is a perfluorinated ($\text{C}_1\text{-}\text{C}_4$)alkyl group, $m = 1\text{-}4$, $n = 0\text{-}6$, and $p = 1\text{-}2$; and
 - b) repeating units derived from vinylidene fluoride; and, optionally,
 - c) an effective amount of cure site moieties derived from one or more compounds of the formulae:
 - i) $\text{CX}_2=\text{CX}(\text{Z})$, wherein:
 - (i) X is H or F; and
 - (ii) Z is Br, I, or R_f^2U wherein $\text{U} = \text{Br}, \text{I}, \text{or CN}$ and $\text{R}_f^2 = \text{a}$ perfluorinated divalent linking group optionally containing O atoms; and
 - ii) $\text{Y}(\text{CF}_2)_q\text{Y}$, wherein:
 - (i) Y is Br or I; and
 - (ii) $q = 1\text{-}6$;
- 10 wherein the polymer has a glass transition temperature of -50°C or lower and an oxygen to carbon ratio of at least about 0.2.
- 20 25 2. The fluorocarbon polymer of claim 1 comprising from 0.2-5 mole-% of the cure site moieties.
3. The fluorocarbon polymer of claim 1 or 2 comprising 50-80 mole-% of the repeating units derived from vinylidene fluoride, and from 10-50 mole-% of the repeating units derived from the Formula I perfluorinated ether.

4. The fluorocarbon polymer of claim 1 or 2 comprising no greater than 30 mole-% of repeating units derived from a fluoromonoolefin other than vinylidene fluoride and the Formula (I) perfluorinated vinyl ether.
5. The fluorocarbon polymer of claim 4 wherein the fluoromonoolefin is tetrafluoroethylene.
6. The fluorocarbon polymer of claim 2 wherein the cure site moieties are derived from one or more compounds selected from the group consisting of $\text{CF}_2=\text{CFBr}$, $\text{ICF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{I}$, $\text{BrCF}_2\text{CF}_2\text{Br}$, $\text{CF}_2=\text{CFO}(\text{CF}_2)_3-\text{OCF}_2\text{CF}_2\text{Br}$, $\text{CH}_2=\text{CHCF}_2\text{CF}_2\text{Br}$, and mixtures thereof, and from one or more compounds of the formula $\text{CF}_2=\text{CFO}(\text{CF}_2)_r\text{OCF}(\text{CF}_3)\text{CN}$ wherein $r = 2-5$.
7. An elastomeric polymer prepared from a crosslinkable composition comprising a fluorocarbon polymer of claim 2, a free radical initiator, and optionally, a co-curing agent.
8. The elastomeric polymer of claim 7 wherein the free radical initiator comprises a peroxide initiator and the co-curing agent comprises a triallyl isocyanurate.
9. An article comprising the elastomeric polymer of claim 7 which is in the form of a seal, a hose, a diaphragm, or a coated substrate.
10. A method of preparing an elastomeric polymer comprising the steps of
 - (a) providing a crosslinkable composition comprising a fluorocarbon polymer of claim 2, optionally a free radical initiator, and optionally a co-curing agent;
 - (b) subjecting the crosslinkable composition to conditions effective to at least partially cure it.
11. The method of claim 10 wherein step (b) comprises applying heat and pressure, or comprises subjecting the composition to radiation.

12. An elastomeric polymer comprising the at least partially crosslinked fluorocarbon polymer of claim 1 or 2.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 99/16561

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08F216/14 C08F214/22

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 290 848 A (DAIKIN IND LTD) 17 November 1988 (1988-11-17) examples 3-8; tables -----	1-6
X	EP 0 774 472 A (BAYER AG) 21 May 1997 (1997-05-21) claims; examples -----	1-10



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
3 November 1999	16/11/1999
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl. Fax: (+31-70) 340-3016	Authorized officer Friederich, P

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inte. onal Application No

PCT/US 99/16561

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